

Let's Take a PEEK at the PEAC Software

PEAC Example–Phosphine

by S. Bruce King

This month our example is Phosphine which has a chemical formula of PH_3 . Phosphine has a United Nations # of 2199 and a Chemical Abstract Service # of 7803-51-2. Phosphine is a colorless, flammable, and toxic gas with an odor of garlic or decaying fish. It can ignite spontaneously on contact with air. The gas is shipped as a liquefied, compressed gas. Aluminum phosphide (Celphos, Phostoxin, Quick Phos, UN# 1397 and CAS# 20859-73-8) and zinc phosphide (UN# 1714 and CAS# 1314-84-7) are solids used as grain fumigants and as a rodenticide, respectively. Zinc phosphide is often mixed with bait food such as cornmeal, which can be a danger to pets and children. When phosphides are ingested or exposed to moisture, they release Phosphine gas. Phosphine gas may also be released when acetylene is made by the action of water on calcium carbide which is contaminated with calcium phosphide as is commonly the case.

For those readers familiar with the US DOT Emergency Response Guide (ERG), at the end of the “green pages” in the back of the ERG are several pages of materials that react with water to form toxic gases. If you notice, Phosphine is one of the toxic gas species listed for a number of phosphide substances in that list. They may not be a toxic hazard by themselves, but on contact with water (or moisture in the air) they can become a concern.

Persons exposed only to Phosphine gas do not pose substantial risks of secondary contamination; however, persons exposed to solid phosphides may present such risks. Metallic phosphides on clothes, skin, or hair can react with water or moisture to generate Phosphine gas. Vomitus containing phosphides can also off-gas Phosphine. Phosphine is extremely flammable and explosive; it may ignite spontaneously on contact, with air. Phosphine has a fish- or garlic-like odor, but may not provide adequate warning of hazardous concentrations. When Phosphine burns it produces a dense white cloud of phosphorus Pentoxide, P_2O_5 fume. This fume is a severe respiratory tract irritant due to the rapid formation of Orthophosphoric acid, H_3PO_4 , on contact with water.

Phosphine is a respiratory tract irritant that attacks primarily the cardiovascular and respiratory systems causing peripheral vascular collapse, cardiac arrest and failure, and pulmonary edema.

Most Phosphine exposures occur by inhalation of the gas or ingestion of metallic phosphides, but dermal exposure to phosphides can also cause systemic effects.

Sources/Uses Phosphine is produced when metallic phosphides (e.g., aluminum, calcium, or zinc phosphides) react with water or acid. Both aluminum and zinc phosphides are used as rodenticides. Phosphine may be produced during the generation of acetylene gas. Phosphine is used in the semiconductor industry to introduce phosphorus into silicon crystals as an intentional impurity. Phosphine is also used as a fumigant and a polymerization initiator.

Synonyms of Phosphine include hydrogen phosphide, phosphorus hydride, phosphorus trihydride, and phosphoretted hydrogen.

Routes of Exposure:

Inhalation Inhalation is the major route of Phosphine toxicity. **Odor is not an adequate indicator of Phosphine's presence and may not provide reliable warning of hazardous concentrations.** The OSHA PEL of 0.3 ppm is within the range of reported odor thresholds. Phosphine is heavier than air and may cause asphyxiation in enclosed, poorly ventilated, or low-lying areas. Children exposed to the same levels of Phosphine as adults may receive a larger dose because they have greater lung surface area:body weight ratios and increased minute volumes:weight ratios. In addition, they may be exposed to higher levels than adults in the same location because of their short stature and the higher levels of Phosphine found nearer to the ground.

Skin/Eye Contact Phosphides may be absorbed dermally, especially through broken skin, and can cause systemic toxicity by this route. Phosphine gas produces no adverse effects on the skin or eyes, and contact does not result in systemic toxicity. Contact with liquefied or compressed Phosphine gas may cause frostbite.

Ingestion Ingestion of Phosphine is unlikely because it is a gas at room temperature. Ingestion of metallic phosphides can produce Phosphine intoxication when the solid phosphide contacts gastric acid.

Physical Properties:

Description: Colorless gas; odor of garlic or decaying fish

Warning properties: Inadequate; nonirritating and garlic-like or fishy odor at 1 to 3 ppm.

Molecular weight: 34.0 daltons

Melting point: -209°F (-134°C)

Boiling point (760 mm Hg): = -126°F (- 87.7°C)

Vapor pressure: >31,300 mm Hg at 68°F (20°C)

Gas density: 1.17 (air = 1)

Water solubility: Slightly water soluble (0.3% at 68°F) (20°C)

Flammability: Extremely flammable and explosive; may ignite spontaneously on contact with air. Lower explosive limit (LEL)=1.8% and upper explosive limit (UEL)=98%.

Standards and Guidelines

OSHA PEL (permissible exposure limit) = 0.3 ppm (averaged over an 8-hour workshift)

NIOSH IDLH (immediately dangerous to life or health) = 50 ppm

Incompatibilities: Phosphine reacts with air, oxidizers, chlorine, acids, moisture, halogenated hydrocarbons, and copper.

Health Effects:

Symptoms of Phosphine intoxication are primarily related to the cardiovascular and pulmonary systems and may include restlessness, irritability, drowsiness, tremors, vertigo, diplopia, ataxia, cough, dyspnea, retrosternal discomfort, abdominal pain, and vomiting.

The same symptoms may occur after ingestion of phosphide salts. Multiple signs may be seen representing various stages of cardiovascular collapse.

Phosphine interferes with enzymes and protein synthesis, primarily in the mitochondria of heart and lung cells. As a result, effects may include hypotension, reduction in cardiac output, tachycardia, oliguria, anuria, cyanosis, pulmonary edema, tachypnea, jaundice, hepatosplenomegaly, ileus, seizures, and diminished reflexes.

Acute Exposure: Phosphine interferes with enzymes and protein synthesis, primarily in the mitochondria of heart and lung cells. Metabolic changes in heart muscle cause cation disturbances that alter transmembrane potentials. Ultimately, cardiac arrest, peripheral vascular collapse and pulmonary edema can occur. Pulmonary edema and pneumonitis are believed to result from direct cytotoxicity to the pulmonary cells. In fatal cases, centrilobular necrosis of the liver has also been reported.

Most deaths occur within the first 12 to 24 hours after exposure and are cardiovascular in origin. If the patient survives the initial 24 hours, the ECG typically returns to normal, indicating that heart damage is reversible. Deaths after 24 hours are usually due to liver failure.

Children do not always respond to chemicals in the same way that adults do. Different protocols for managing their care may be needed.

CNS Phosphine is a CNS depressant. Initial effects may include headache, restlessness, dizziness, loss of feeling, impaired gait, trembling of the extremities during movement, and double vision.

Respiratory Toxicity that occurs after inhalation is characterized by chest tightness, cough, and shortness of breath. Severe exposure can cause accumulation of fluid in the lungs, which may have a delayed onset of 72 hours or more after exposure. Pulmonary symptoms can also result from ingestion of metallic phosphides (e.g., aluminum or zinc phosphide).

Children may be more vulnerable because of relatively increased minute ventilation per kg and failure to evacuate an area promptly when exposed.

Cardiovascular Cardiovascular manifestations include hypotension, reduction in cardiac output, tachycardia, irregular heart beat, or cardiac arrest. Laboratory tests may reveal abnormal myocardial enzymes. Phosphine affects the small peripheral vessels,

causing a profound decrease in systemic vascular resistance. Vascular changes may lead to marked low blood pressure that does not respond well to pressor agents.

Gastrointestinal Gastrointestinal symptoms are usually the first to occur after exposure. Symptoms may include nausea, vomiting, abdominal pain, and diarrhea.

Hepatic Typically, liver injury does not become evident until 48 to 72 hours after exposure. Findings may include jaundice, enlarged liver, elevated serum transaminases, and increased bilirubin in the blood.

Renal Blood and protein in the urine, and acute kidney failure can occur.

Electrolyte Analysis of blood gases may reveal combined respiratory and metabolic acidosis. Also, there have been reports of significant hypomagnesemia and hypermagnesemia associated with massive focal myocardial damage.

Potential Sequelae Although most survivors of acute Phosphine exposure show no permanent disabilities, damage due to insufficient blood supply to the heart and brain have been reported. Subacute poisoning resulting from exposure for a few days may cause reactive airways dysfunction syndrome (RADS) months later.

Chronic Exposure Chronic exposure to very low concentrations may result in anemia, bronchitis, gastrointestinal disturbances, and visual, speech, and motor disturbances. Chronic exposure may be more serious for children because of their potential longer latency period.

Carcinogenicity The EPA has determined that Phosphine is not classifiable as to its human carcinogenicity.

Reproductive and Developmental Effects Phosphine is not contained in the TERIS or Reprotext databases, nor is it mentioned in *Shepards Catalog of Teratogenic Agents*. Phosphine is not included in *Reproductive and Developmental Toxicants*, a 1991 report published by the U.S. General Accounting Office (GAO) that lists 30 chemicals of concern because of widely acknowledged reproductive and developmental consequences.

No teratogenic effects from acute exposure are known.

In using the PEAC application we access information for the chemical by first locating Phosphine in the database. The following figures show the screens displayed for chemical properties, Figure 1 for the *PEAC-WMD for Windows* application and Figure 2-5 for the *PEAC-WMD for the Pocket PC* application.

PEAC-WMD

File Edit Tools Help

Lookup By: **Chemical Name**

Lookup: **Phosphine**

Chemical Properties

Phosphine

GUIDE 119 Gases - Toxic - Flammable
UN 2199

Colorless gas; garlic odor; danerous fire hazard from spontaneous chemical reaction

Formula: PH₃

Shipped as liquefied gas under its own vapor pressure.
WARNING: This material ignites in contact with air or water. The results given here DO NOT provide for the reaction with air or water.
May only be shipped in cylinders without safety release and overpacked in metal or wooden containers.
If heat or rupture, will rocket.

NFPA Information
Health: 4 Deadly
Fire: 4 Flash Point < 73°
Reactivity: 2 Violent Chemical Change

CAS NO: 7803-51-2
Lower Explosive Limit: 1.8%
Upper Explosive Limit: 98%
Boiling Point: -126°F
Melting Point: -209°F
Rel Vapor Density @68°F: 1.2
Vapor Pressure @68°F: 41.3 atm
Liquid Specific Gravity: 0.76
Ionization Potential: 9.87 eV
Molecular Weight: 34
IDLH: 50 ppm
TWA: 0.3 ppm
STEL: 1 ppm
ERPG2: 2.5 ppm

Phosphine, (difluoro)methyl-
Phosphine, dichloroethyl-
Phosphinic acid
Phosphonic acid, diethyl ester
Phosphonic acid, ethyl-, diethyl ester
Phosphonic acid, methyl-, diethyl ester
Phosphonic dichloride, methyl-
Phosphonic difluoride, methyl-
Phosphonochloridic acid
Phosphonodifluoridic acid, methyl-
Phosphonodithioic acid, ethyl-, O-ethyl S-phenyl ester
Phosphonofluoridic acid, ethyl-, 1-methylethyl ester
Phosphonofluoridic acid, ethyl-, isopropyl ester
Phosphonofluoridic acid, methyl-, 1-methylethyl ester
Phosphonofluoridic acid, methyl-, isopropyl ester
Phosphonofluoridic acid, methyl-, 1,2,2-trimethylpropyl ester
Phosphonothioic acid methyl-, S-(2-Bis(1-Methylethyl)Amino)E
Phosphonothioic acid, methyl-

Phosphoric chloride
Phosphoric sulfide
Phosphoric trichloride
Phosphorothioic Trichloride
Phosphorous Acid

Phosphine

Select **Lookup By** chemical name

Key in the name of the chemical

The NFPA 704 Hazard Classification system immediately identifies the material as a health and fire hazard.

Additional information provided below the specific information regarding its properties, including the fire and toxicity hazard. Additional toxicity information can be viewed by scrolling further down the screen.

Figure 1 - Using the Lookup By: Name for Phosphine using the PEAC-WMD for Windows Application

Review of the information displayed in the chemical properties screen whether in Figure 1 (above) or Figures 2-5 (below), show chemical properties values discussed earlier at the top of this discussion. In addition, other values are provided such as the TEELs (Temporary Emergency Exposure Limit) published by Department of Energy.

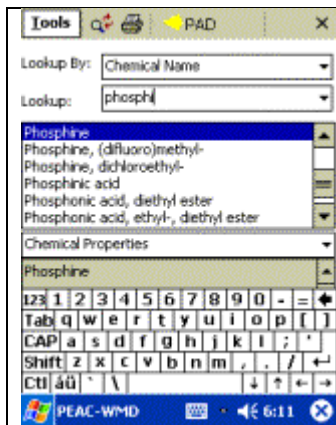


Figure 2 – Selecting Phosphine using the PEAC-WMD for Pocket PC application

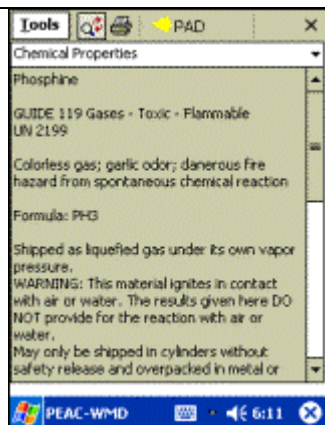


Figure 3 – The top portion of the Chemical Properties Data Display Screen

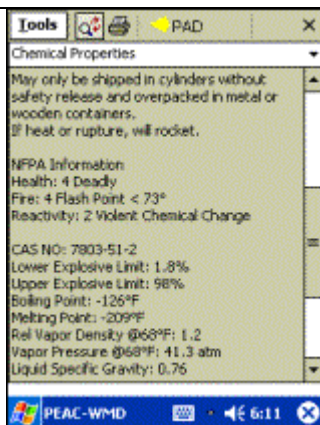


Figure 4 – The middle portion of the Chemical Properties Data Display Screen

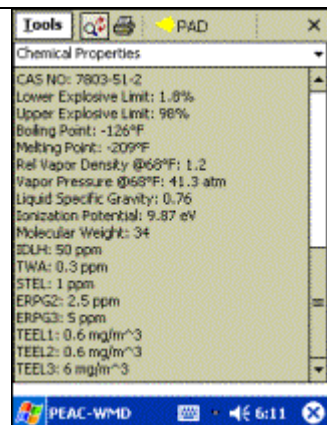


Figure 5 – The bottom portion of the Chemical Properties Data Display Screen

An advantage of using the PEAC tool is assistance in the development of an evacuation zone for those chemicals that produce a toxic vapor cloud. Phosphine has a very high vapor pressure (>40 atm), and with a boiling point of -126°F it is usually shipped as a liquefied gas under its own vapor pressure. When such a container is breached or vented, the material is going to be released as a vapor or aerosol and rapidly form a vapor cloud.

As with all of our examples, AristaTek creates a scenario for a spill or release of the specific chemical and then we work through the development of a PAD (Protective Action Distance) to demonstrate how the PAD calculation portion of the PEAC system works. For our scenario using Phosphine as the spilled chemical we'll use a computer chip manufacturing facility in San Jose, CA that has a pressurized storage tank containing Phosphine positioned next to a building that has 1/2" feed line from the tank to the building broken and releasing vapor. It's 6:30 PM on July 2nd, the temperature is about 80°F, the winds are 5 mph, and it's a partly cloudy day.

As seen at the top of the data display screens, there is a yellow icon displayed, this is the PEAC icon for notifying the user that a Protective Action Distance can be calculated. Clicking or tapping on the PAD icon will display a screen as shown in Figure 6. Following through the screens, we provide information on the Meteorology, Container Size, and Type of Release (Source). The last screen displays the PAD based on the provided information.

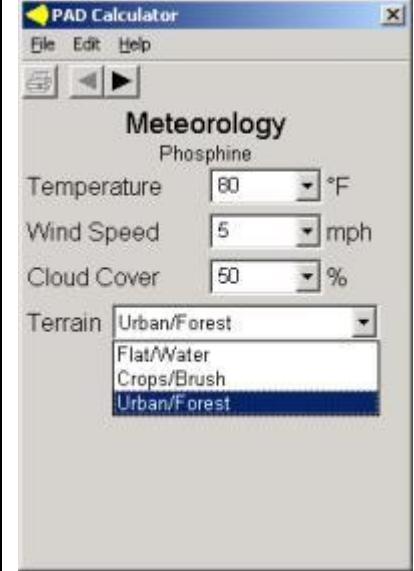
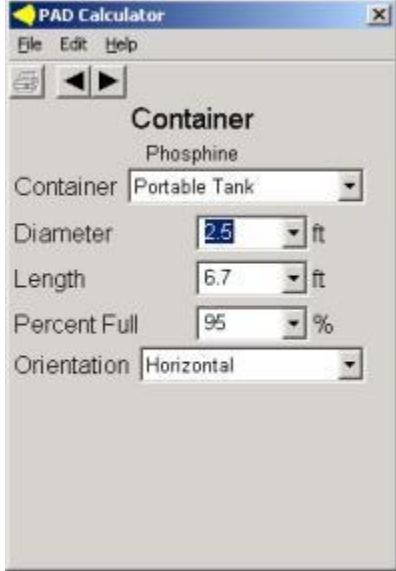

 <p>Meteorology Phosphine</p> <p>Temperature: 80 °F Wind Speed: 5 mph Cloud Cover: 50 % Terrain: Urban/Forest</p>	 <p>Container Phosphine</p> <p>Container: Portable Tank Diameter: 2.5 ft Length: 6.7 ft Percent Full: 95 % Orientation: Horizontal</p>	 <p>Source Phosphine</p> <p>Source Type: Hole or Pipe Release Release Hole Hole Diameter: 1.5 in Hole Height: 0 ft</p>
<p>Meteorology</p> <p>It's San Jose in July and the temperature about 80°, wind is set for 5 mph, partly cloudy so we'll set cloud cover to 50%, and the terrain is Urban/Forest since it's an urban setting (manufacturing facility).</p>	<p>Container</p> <p>We have selected from our list of container sizes the Portable Tank selection. This is smaller than a tanker trailer but bigger than a drum or barrel.</p>	<p>Source</p> <p>Since the scenario has Phosphine released from a broken transfer line Hole or Pipe Release as the Source type.</p>

Figure 6 – Calculating a PAD using the PEAC System

After specifying the release or source is a **Hole or Pipe Release**, the user taps the right arrow at the top of the screen and the PAD computation results are displayed, see Figure 7.

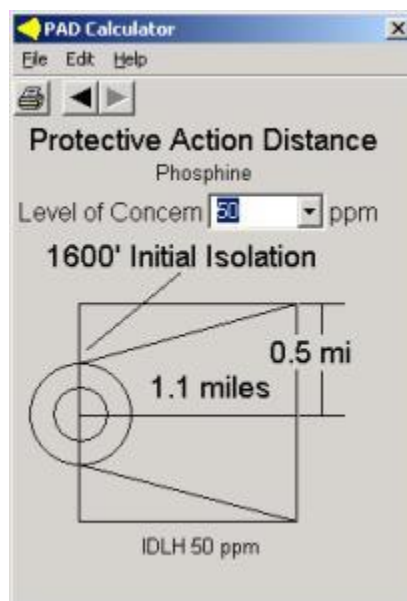


Figure 7 - The PEAC computation for PAD using the IDLH

Portions of this discussion on Phosphine were adapted from the ATSDR Medical Management Guideline document, which can be downloaded from the ADSTR web site at: <http://www.atsdr.cdc.gov/mmg.html>.